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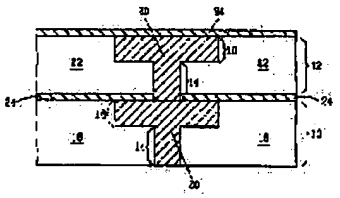
(54) FORMATION OF COPPER INTERCONNECTION STRUCTURE

(57)Abstract:
PROBLEM TO BE SOLVED: To improve adhesiveness of a deposited inorganic barrier film to a copper surface of a copper interconnection structure by including exposure of a copper layer in an interconnected semiconductor structure to a reducing plasma before the formation of the inorganic barrier film on the copper interconnection structure.
SOLUTION: A copper interconnection structure is exposed to a reducing plasma before an inorganic barrier film 24 is deposited. This reducing plasma is a non-oxidizing, i.e., oxygen-atom-free plasma atmosphere. A suitable plasma is selected from H2, N2, NH3, and rare gas, but it is not limited to these. Further, a combination of more than two of these reducing plasmas such as N2 and H2 is intended. N2 and NH3 are very preferable among these reducing plasmas. The adhesiveness of the inorganic barrier layer 24 to copper 20 can be improved by using this reducing plasma exposure process.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention is the copper wire of especially such interconnection structure, or Si 3N4 to copper Bahia about interconnection semiconductor structure. It is related with the method of improving the adhesive property of an inorganic barrier film [like]. In this specification, a term "interconnection structure" is a latus meaning and is used as a thing including all the semiconductor structures of having copper interconnection METARAJI (metallurgy). therefore, this invention is applicable to the use in other wiring application for a pellet syn conformation (a single -- and dual), a memory cell capacitor and logic, memory, and input/output application
[0002]
[Description of the Prior Art] In semiconductor industry, aluminum and the aluminium alloy have been used as conventional interconnection METARAJI. Although METARAJI which uses aluminum as the base is a selection material used as metaled interconnection over past many years, the problem whether aluminum agrees now in the demand needed with increase of the circuit density of a semiconductor device and circuit speed exists. For these increasing problems, other materials have been examined as a possible alternative to METARAJI which uses aluminum as the base. One of the very advantageous material considered as a possible alternative to aluminum METARAJI now is copper. This is because copper shows low susceptibility and low resistivity further to an electromigration obstacle compared with aluminum.
[0003] In spite of these advantages, copper has the problem that it is easily spread into surrounding dielectric materials in the case of subsequent down stream processing. In order to avoid copper diffusion, in many cases, it acts as the cap of the copper interconnection section in a protection barrier layer. One of the methods of acting as a cap includes use of the conductive barrier layer which consists of the tantalums or titanium in alignment with the side attachment wall and pars basilaris ossis occipitalis of the copper interconnection section, or those alloys. In order to act as the cap of the upper surface of the copper interconnection section, dielectric materials like a silicon nitride (Si 3N4) are used typically.
[0004] Since it is necessary to carry out low temperature treatment after adhesion of copper, it adheres to a silicon-nitride layer at the temperature of 450 degrees C or less. Therefore, adhesion of a silicon nitride is typically performed using a plasma excitation chemical-vapor-deposition method (PECVD) or a high-density plasma-chemistry vapor growth (HDPCVD). Generally by these methods, adhesion temperature is about 200 - 500 degrees C of abbreviation.
[0005] The silicon nitride of PECVD and HDPCVD has been used for many of other application in semiconductor-device industry. However, when using a silicon-nitride cap (protective coat) for the copper interconnection section, the silicon nitride of the usual PECVD or HDPCVD produces the problem of reliability. Especially the silicon nitride film to which it adhered using the usual PECVD or HDPCVD processing shows the adhesive property which was generally inferior to the copper front face. For example, in the case of adhesion of subsequent dielectrics, metallization, and chemical machinery polish, especially the nitride of a certain portion exfoliates and forms a blister (blister) after the copper wiring by which patterning was carried out.
[0006] These results show the grade which a silicon nitride film can paste up to copper in the actual manufacture process. After adhering on copper METARAJI, generally it adheres to an insulating layer on a silicon nitride film. However, adhesion of the insulating layer to a nitride top produces stress, and this stress makes a silicon nitride film exfoliate from a copper front face. This exfoliation produces the lift of the dielectric between metals, the lift of copper wire, and some destructive obstacle mechanisms including the copper diffusion from copper wire which does not act as a cap. Generally such a result is seen in dual DAMASHIN processing. Generally in dual DAMASHIN processing, exfoliation of a silicon-nitride RIE halt layer arises in the case of copper chemical machinery polish (CMP).
[0007] The adhesive property of the nitride to the copper of the conventional technology needs to silicide-ize a copper front face by making copper react with silicon. The method of this conventional technology has two faults. namely, the thing increased in copper sheet resistance for the silicon which reacts with copper and is diffused in copper -- and imperfect -- again -- ** -- for formation of partial copper silicide, I hear that a limitation is in the adhesive property of the nitride to copper, and it is in it
[0008] The need of developing the new method of increasing the adhesive property of the inorganic barrier film to the copper front face which exists in interconnection semiconductor structure for the fault mentioned above about the copper interconnection structure of the conventional technology still exists.

[0009]
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the method of improving the adhesive property of the adhesion inorganic barrier film to the copper front face of interconnection structure.
[0010] Other purposes of this invention have an adhesion inorganic barrier film in offering the method which does not exfoliate from the copper front face of interconnection structure in the case of subsequent interconnection down stream processing.
[0011] The purpose of everything but this invention furthermore is Si 3N4 to copper wiring or copper Bahia. It is in offering the method of using for dual DAMASHIN processing in which the adhesive property of an etching halt layer is improved.
[0012]
[Means for Solving the Problem] Before forming an inorganic barrier film for these, and other purposes and advantages on copper interconnection structure in this invention, it can attain by using a method including the process which exposes the layer of the copper within interconnection semiconductor structure to reduction plasma. especially the method of this invention of improving the adhesive property of the adhesion inorganic barrier film on the copper front face of interconnection structure -- (a) -- the process which exposes the interconnection semiconductor structure of having the layer of at least one copper to reduction plasma, and the process which forms an inorganic barrier film on the copper interconnection structure where it was exposed to the (b) aforementioned plasma are included
[0013] According to the method of this invention, an exposure process (a), i.e., a process, is performed within the plasma containing at least one sort of non-oxidizing gas chosen from the group which consists of rare gas like H2, N2, NH3, and helium, Ne, Ar, Kr and Xe, and those mixture. Since the copper which exists in interconnection structure is oxidized and the nitride of a copper interface is degraded, as for an oxidizing atmosphere, it turns out that an oxidizing atmosphere is excepted from this invention.
[0014] Although the suitable interconnection structure meant in this invention includes the multilayer-interconnection level which has the memory cell capacitor and single which have a monotonous capacitor, crown KYAPASHI, a stack capacitor, and other same capacitors and a dual pellet syn conformation, two or more Bahia, and a metal wire, and other same interconnection structures, it is not restricted to these.
[0015]
[Embodiments of the Invention] This invention that is the method of improving the adhesive property of the adhesion inorganic barrier film on the copper front face which exists in interconnection semiconductor structure is explained more to a detail with reference to drawing 1 . Although this invention explains only a dual pellet syn conformation, it has copper METARAJI, and it is SiC or Si 3N4 as a protection barrier or an etching halt layer. It emphasizes that it is applicable to all the interconnection semiconductor structures using an adhesion inorganic barrier film [like].
[0016] Drawing 1 shows the typical dual pellet syn conformation which can apply the method of this invention. Especially this dual pellet syn conformation has the lower interconnection level 10 and the up interconnection level 12. Each level has the Bahia field 14 and a metal wire, or the wiring field 16. The lower interconnection level 10 has the dielectric 18 which has opening or a trench (it fills up with copper 20). There is up interconnection level 12 in the upper part of the lower interconnection level 10, and this level has the dielectric 22 with the trench field which leads to copper wiring of lower interconnection level. The trench field of the up interconnection level 12 is filled up with copper 20. A RIE halt layer, a protection barrier film, or the inorganic barrier layer 24 that serves as both them is between each interconnection level.
[0017] Before the dual pellet syn conformation shown in drawing forms the barrier layer 24, it is produced by this contractor using well-known typical DAMASHIN down stream processing except for applying the method (later explained more to a detail) of this invention to interconnection structure.
[0018] Let dielectric layers 18 and 22 be the same, different insulating inorganic material, or an organic material. Although a suitable dielectric contains SiO2, fluoride SiO2, Si 3N4, polyimide, diamond, and diamond-like carbon, silicon polymer, Para Lynn (paralyne) polymer, fluoride diamond-like carbon, and other same dielectric compounds, it is not restricted to these. the dielectric layers 18 and 22 among these dielectric materials -- SiO2 from -- changing is desirable a dielectric layer dopes -- it is -- it is -- it cannot dope, either When you dope, let a dopant be boron, a fluorine, Lynn, heavy hydrogen, silicon, germanium (germanium), or other same dopants.
[0019] The barrier layer 24 is inorganic material which serves as a protection barrier layer, when it serves as a RIE halt layer for Bahia or exists as an outermost layer of drum of structure. Although a suitable material for the barrier layer 24 includes Si 3N4, SiC, hydrogenation Si 3N4, and Hydrogenation SiC, it is not restricted to these. In this invention, it is desirable among such material to use Si 3N4 of a hydrogenation gestalt and SiC as a barrier layer. Moreover, an alternative RIE halt layer can also be inserted between a metal wire 16 and Bahia 14 (this example is not shown in a drawing).
[0020] The barrier layer 24 is formed using the usual vapor-growth method. Although the usual vapor-growth method contains a chemical-vapor-deposition method, a low voltage chemical-vapor-deposition method, a piezochemistry vapor growth, a high-density plasma-chemistry vapor growth, a plasma excitation chemical-vapor-deposition method, and other same vapor growths, it is not restricted to these. A plasma excitation chemical-vapor-deposition method (PECVD) and a high-density plasma-chemistry vapor growth (HDPCVD) are the suitable methods of adhering a barrier layer among these adhesion methods.
[0021] It emphasizes once again that the dual pellet syn conformation shown in a drawing and all the copper interconnection structures considered by others are produced by this contractor using the well-known method. Such a method is common

knowledge, and since it is not serious in order to understand this invention, it does not have the same detailed discussion here. the only difference in producing the interconnection structure of this invention and the interconnection structure of the conventional technology is exposing copper interconnection structure to reduction plasma by the condition lower defined below, before adhering the inorganic barrier layer 24

[0022] Especially the reduction plasma used in this invention does not oxidize, namely, is a plasma atmosphere which does not contain an oxygen atom. Although the suitable reduction plasma used in this invention contains H2, N2, NH3, and rare gas, it is not restricted to these. Moreover, N2 And H2 Two or more sorts of combination [like] of such reduction plasma is also meant. H2 among such reduction plasma And NH3 is very suitable in this invention.

[0023] The reduction plasma exposure process of this invention is performed by the usual plasma adhesion equipment which can generate plasma gas. Especially the exposure process of this invention is performed at the temperature of about 20 - 600 degrees C of abbreviation during the period for about 1 - about 3600 seconds. Moreover, an exposure time longer than 3600 seconds is also meant. The exposure process of this invention is performed at the temperature of about 360 - 400 degrees C of abbreviation during the period for about 5 - about 30 seconds still more preferably. Preferably, heating is performed under existence of reduction plasma.

[0024] Furthermore, the exposure process of this invention is performed by the pressure of about 1 mTorr - about 20 Torr(s), the power of abbreviation 50 - about 10,000 W, and the quantity of gas flow of about 1 - about 10,000 sccm(s). Strict conditions are based on the kind of adhesion processing used for formation of a barrier layer. for example, the case where a high-density plasma-chemistry vapor growth (HDPCVD) is used -- the exposure process of this invention -- the pressure of about 3 - about 6 mTorr(s), and about 1500- about 3000 -- it is carried out by the power of W, and the quantity of gas flow of about 10 - about 50 sccm(s) the time of on the other hand a plasma excitation chemical-vapor-deposition method (PECVD) being used -- the exposure process of this invention -- the pressure of about 2 - about 8 Torr(s), and about 150- about 400 -- it is carried out by the power of W, and the quantity of gas flow of about 100 - about 2000 sccm(s)

[0025] Note that an inorganic barrier layer is formed on copper immediately after an exposure process using either of the adhesion methods mentioned above, without interrupting a vacua. The method of this invention and the copper interconnection structure where, especially as for a reduction plasma exposure process, an inorganic barrier layer has the improved adhesive property over copper wiring or copper Bahia, without being obtained with the conventional technology until now and reliance also making resistance increase are given. Therefore, since an adhesive property is improved using the method of this invention, the copper interconnection structure formed in this way does not show the problem of all ablation usually faced with the interconnection structure of the conventional technology in the case of down stream processing of henceforth like chemical machinery polish. Furthermore, the interconnection structure manufactured using the method of this invention hardly shows those increases in resistance.

[0026] It gives in order to explain the range of this invention, and the following examples are ****. Since this example is given in order to illustrate only carried-out invention, this invention is not restricted to this example.

[0027]

[Example] A series of experiments in order to explain the adhesive property by which it was improved between the inorganic vapor-growth barrier layers and copper wiring which are obtained using the method of this invention are SiO2. It was carried out inside on 200mm Si wafer which has the copper wire produced by DAMASHIN. Especially, it is Si 3N4 on copper wiring of a dual pellet syn conformation. Before adhering, except for the front face having been processed using various methods including no processing (CE1), processing (CE2) within oxidization plasma-gas atmosphere, or processing within the reduction plasma by the method of this invention, the dual pellet syn conformation was prepared using standard DAMASHIN processing conditions. The processing before adhesion, and Si 3N4 Each structure was optically investigated about ablation after adhesion, the adhesion between metals, and dual DAMASHIN copper wiring / copper Bahia production. The result of these experiments is summarized in the following table 1. In Table 1, it is indicated to be "good" that there is almost no ablation substantially, namely, the adhesive property is improved and the "defect" shows that there is no adhesive property substantially. Moreover, in connection with the adhesive property of a nitride having been improved, it was also observed that the copper front face became still more nearly reflecting.

[0028]

[Table 1]

Si_3N_4付着前の処理	圧力	高周波出力 (W)	電極	温度 (℃)	付着Si_3N_4接着性	CMP後のSi_3N_4接着性	434nmの反射率
無処理 (CE1)	–	–	–	–	不良	不良	0.50
PECVD NH_3	5 Torr	300	1 cm 平行平板	260	良	良に近い	0.68
PECVD NH_3	5 Torr	300	1 cm 平行平板	400	良	良に近い	0.58
PECVD N_2	5 Torr	300	1 cm 平行平板	250	良	不良	測定不能
PECVD N_2O+N_2 (1:1) (CE2)	5 Torr	300	1 cm 平行平板	250	不良	不良	測定不能
HDPCVD N_2+H_2	5 mTorr	2000	誘導結合	375	良	良	0.55
HDPCVD H_2	5 mTorr	2000	誘導結合	375	良	良	0.63
HDPCVD N_2	5 mTorr	2000	誘導結合	375	良	良	0.69
HDPCVD NH_3	5 mTorr	2000	誘導結合	375	良	不良	0.53

[0029] The above-mentioned result is Si 3N4 to copper by using the reduction plasma exposure process of this invention. It is shown clearly that the adhesive property by which the barrier layer was improved can be acquired. In the example of comparison (CE1 and CE2), an adhesive property is inferior, and it is Si 3N4. Ablation of an adhesion film was observed.
[0030] Although this invention was explained about the suitable example of this invention, it will be understood by this contractor that a gestalt and the above-mentioned which can be set in detail are performed, and other change can be made, without deviating from the main point and range of this invention.
[0031] As a conclusion, the following matters are indicated about the composition of this invention.
(1) The method characterized by including the process which exposes the interconnection semiconductor structure of having the layer of (a) copper to reduction plasma in the formation method of copper interconnection structure, and the process which forms an inorganic barrier film on the copper interconnection structure by which the (b) aforementioned exposure was carried out.
(2) A method given in (1) characterized by performing the aforementioned exposure process within non-oxidizing [which was chosen from the group which consists of H2, N2, NH3, rare gas, and those mixture] plasma atmosphere.
(3) the aforementioned non-oxidizing plasma atmosphere -- H2 it is -- method given in (2) characterized by things
(4) the aforementioned non-oxidizing plasma atmosphere -- NH3 it is -- method given in (2) characterized by things
(5) the aforementioned exposure process -- the period for about 1 - about 3600 seconds or a period longer than 3600 seconds, and about 20- a method given in (1) characterized by carrying out at the temperature of about 600 degrees C
(6) A method given in (5) characterized by performing the aforementioned exposure process at the temperature of about 360 - 400 degrees C of abbreviation during the period for about 5 - about 30 seconds.
(7) the aforementioned exposure process -- about 1mTorr- the pressure of about 20 Torr(s), and about 50- about 10,000 -- the power of W, and a method given in (1) characterized by carrying out by the quantity of gas flow of about 1 - about 10,000 sccm(s)
(8) the aforementioned exposure process -- the pressure of about 3 - about 6 mTorr(s), and about 1500- about 3000 -- a method given in (1) characterized by carrying out by the high-density plasma-chemistry vapor growth by the power of W, and the quantity of gas flow of about 10 - about 50 sccm(s)
(9) the aforementioned exposure process -- the pressure of about 2 - about 8 Torr(s), and about 150- about 400 -- a method given in (1) characterized by carrying out by the plasma excitation chemical-vapor-deposition method by the power of W, and the quantity of gas flow of about 100 - about 2000 sccm(s)
(10) The aforementioned copper interconnection structure is a method given in (1) characterized by being the multilayer-interconnection level which has capacitor structure, a pellet syn conformation or two or more Bahia, and a metal wire.
(11) A method given in (10) characterized by being the single or dual pellet syn conformation which has copper wire and copper Bahia for the aforementioned copper interconnection structure.
(12) A method given in (1) characterized by forming the aforementioned inorganic barrier film on that spot using the adhesion processing chosen from the group which consists of a chemical-vapor-deposition method, a low voltage chemical-vapor-deposition method, a plasma excitation chemical-vapor-deposition method, and a high-density plasma-chemistry vapor growth.
(13) A method given in (12) characterized by forming the aforementioned inorganic barrier film on that spot by the plasma excitation chemical-vapor-deposition method or the high-density plasma-chemistry vapor growth.
(14) The aforementioned inorganic barrier film is a method given in (1) characterized by the bird clapper from Si 3N4, SiC, hydrogenation Si 3N4, or Hydrogenation SiC.
(15) The aforementioned inorganic barrier film is hydrogenation Si 3N4. Or method given in (14) characterized by being Hydrogenation SiC.
(16) The aforementioned interconnection structure is a method given in (1) characterized by having the dielectric materials chosen from the group which consists of SiO2, fluoride SiO2, Si 3N4, polyimide, diamond, and diamond-like carbon, silicon polymer, PARARIN polymer, and fluoride diamond-like carbon.
(17) the aforementioned dielectric materials -- SiO2 it is -- method given in (16) characterized by things
(18) The layer of the aforementioned copper is a method given in (1) characterized by being formed in the interior of a trench.

(19) The method given in (1) characterized by the adhesive property of the aforementioned inorganic barrier film formed on the aforementioned copper interconnection structure increasing by the aforementioned exposure.

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CLAIMS

[Claim(s)]
[Claim 1] The method characterized by including the process which exposes the interconnection structure of having the layer of (a) copper to reduction plasma in the formation method of copper interconnection structure, and the process which forms an inorganic barrier film on the copper interconnection structure by which the (b) aforementioned exposure was carried out.
[Claim 2] The method according to claim 1 characterized by the adhesive property of the aforementioned inorganic barrier film formed on the aforementioned copper interconnection structure increasing by the aforementioned exposure.
[Claim 3] The method according to claim 1 characterized by performing the aforementioned exposure process within non-oxidizing [which was chosen from the group which consists of H2, N2, NH3, rare gas, and those mixture] plasma atmosphere.
[Claim 4] the aforementioned non-oxidizing plasma atmosphere -- H2 it is -- method according to claim 3 characterized by things
[Claim 5] the aforementioned non-oxidizing plasma atmosphere -- NH3 it is -- method according to claim 3 characterized by things
[Claim 6] The method according to claim 1 characterized by performing the aforementioned exposure process at the temperature of about 20 - 600 degrees C of abbreviation during the period for about 1 - about 3600 seconds.
[Claim 7] The method according to claim 6 characterized by performing the aforementioned exposure process at the temperature of about 360 - 400 degrees C of abbreviation during the period for about 5 - about 30 seconds.
[Claim 8] The method according to claim 1 characterized by performing the aforementioned exposure process by the pressure of about 1 mTorr - about 20 Torr(s), the power of abbreviation 50 - about 10,000 W, and the quantity of gas flow of about 1 - about 10,000 sccm(s).
[Claim 9] The method according to claim 1 characterized by performing the aforementioned exposure process by the high-density plasma-chemistry vapor growth by the pressure of about 3 - about 6 mTorr(s), the power of abbreviation 1500 - about 3000 W, and the quantity of gas flow of about 10 - about 50 sccm(s).
[Claim 10] The method according to claim 1 characterized by performing the aforementioned exposure process by the plasma excitation chemical-vapor-deposition method by the pressure of about 2 - about 8 Torr(s), the power of abbreviation 150 - about 400 W, and the quantity of gas flow of about 100 - about 2000 sccm(s).
[Claim 11] The method according to claim 1 characterized by forming the aforementioned inorganic barrier film on that spot using the adhesion processing chosen from the group which consists of a chemical-vapor-deposition method, a low voltage chemical-vapor-deposition method, a plasma excitation chemical-vapor-deposition method, and a high-density plasma-chemistry vapor growth.
[Claim 12] The method according to claim 11 characterized by forming the aforementioned inorganic barrier film on that spot by the plasma excitation chemical-vapor-deposition method or the high-density plasma-chemistry vapor growth.
[Claim 13] The aforementioned inorganic barrier film is a method according to claim 1 characterized by the bird clapper from the material chosen from Si 3N4, SiC, hydrogenation Si 3N4, and the group that becomes hydrogenation SiC.
[Claim 14] The aforementioned inorganic barrier film is hydrogenation Si 3N4. Or method according to claim 13 characterized by being Hydrogenation SiC.
[Claim 15] The aforementioned interconnection structure is a method according to claim 1 characterized by having the dielectric materials chosen from the group which consists of SiO2, fluoride SiO2, Si 3N4, polyimide, diamond, and diamond-like carbon, silicon polymer, PARARIN polymer, and fluoride diamond-like carbon.
[Claim 16] the aforementioned dielectric materials -- SiO2 it is -- method according to claim 15 characterized by things
[Claim 17] The layer of the aforementioned copper is a method according to claim 1 characterized by being formed in the interior of a trench.

[Translation done.]